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Abstract of the disclosure:

Aqueous copolymer dispersions can be prepared from styrene, methyl methacrylate, esters of acrylic acid, hydroxyalkyl (meth)acrylates, unsaturated monocarboxylic or dicarboxylic acids, acrylamide and/or methacrylamide, N-methylolacrylamide and/or N-methylolmethacrylamide or etherified N-methylol(meth)acrylamides, when the monomers and the ratios of their amounts are specifically selected, by copolymerization in the presence of an emulsifier and a radical-forming initiator, which dispersions, in combination with aminoplast resins, provide thermosetting coating agents with outstanding properties. These coating agents provide surface coatings which have high elasticity, resistance to weathering, good adhesion and freedom from flaws.

The invention relates to a process for the preparation of an aqueous copolymer dispersion and the use of this dispersion for the preparation of coatings which can be crosslinked by heat (thermosetting coatings).

5 Aqueous copolymer dispersions are of particular interest for the preparation of thermosetting coatings, because they are not flammable and are less physiologically objectionable than coating agents containing solvents. Furthermore, there is no necessity to recover a costly
10 solvent. In addition to the properties which are required of all plastics dispersions, such as good flow behavior and thus processability, freedom from coagulation, storage and heat stability, it is also particularly important for copolymer dispersions which are to be used as binders for
15 the preparation of thermosetting coatings that coating agents are obtained which are readily pigmented and adhere well, which dry even at room temperature and which show no cracks or other irregularities in the film. The coatings obtained from these should then be curable by heat treat-
20 ment. For this purpose, the copolymers on which the dispersions are based have reactive groups in the molecule which react with reactive groups of certain resins, in particular aminoplast resins, so that the binder crosslinks.

In addition to the advantages such as, for example,
25 low viscosity at a high content of solids, high molecular weight and the absence of volatile solvents, aqueous copolymer dispersions also have disadvantages for thermosetting coatings such as, for example, a lack of pigment wetting, a deficient pigment binding capacity and a lack



of adhesion to the substrate by the coating agents prepared by means of this dispersion and an inadequate elasticity of the baked films.

Mixtures of aqueous polyacrylate dispersions with
5 polyepoxides as the reactive partner are known (cf. German Auslegeschrift 1,199,420 = British Patent 848,350). Lacquer films of these mixtures become brittle on weathering and turn yellow under the action of UV light.

Copolymers in aqueous dispersion which are
10 mainly produced from α,β -unsaturated carbonitriles and which can be crosslinked with amino- or phenol-formaldehyde condensation products are also known (cf. German Auslegeschrift 1,248,194). However, these products are unsuitable as binders for high-quality lacquers for metals,
15 since the lacquer films prepared from them do not fulfil practical requirements in respect of the tendency to turn yellow, flexibility and adhesion.

Aqueous copolymer dispersions are also known in which the copolymers on which they are based contain monomer units which have hydroxyl groups but no nitrogen (cf.
20 German Offenlegungsschrift 2,252,065 = U.S. Patent 4,132,688). By means of these dispersions, the gloss and the scratch resistance of the lacquer films prepared from them can admittedly be improved, but, even in this case,
25 the flexibility of the lacquer films is inadequate for practical requirements.

Moreover, aqueous copolymer dispersions are known, for the preparation of which aromatic monovinyl monomers are copolymerized with esters of acrylic or methacrylic

acid and monomers having hydroxyl, amide, amine, carboxyl or epoxide groups (cf. German Offenlegungsschriften 2,211,169 and 2,709,308 = U.S. Patents 3,962,167 and 4,020,219 and British Patent 1,574,721). However, these
5 dispersions cannot be converted by customary recipes into high-quality thermosetting white lacquers, since, after baking, lacquer films are obtained which have blisters, low gloss and inadequate resistance to chemicals.

The object of the invention is to make an aqueous
10 dispersion of a copolymer which can be crosslinked with an aminoplast resin under the action of heat, and which leads to particularly flexible and flawless coatings for metallic substrates.

It has now been found that an aqueous copolymer
15 dispersion can be prepared from styrene, esters of acrylic and/or methacrylic acid, acrylic and/or methacrylic acid, acrylamide and/or methacrylamide, N-methylolacrylamide and/or N-methylolmethacrylamide, when the monomers and the ratios of their amounts are selected in a certain manner,
20 by polymerization in the presence of an anionic and, if appropriate, a non-ionic emulsifier and a radical-forming initiator, which dispersion in combination with an aminoplast resin provides thermosetting coatings with exceptional properties. These coatings provide highly elastic
25 weather-resistant surface coatings which have good adhesion and are free of flaws on metallic substrates.

The invention relates to a process for the preparation of an aqueous dispersion of copolymers, which can be crosslinked with aminoplasts by the action of heat, by

copolymerization of styrene and/or methyl methacrylate as the "hardening" component, 2-ethylhexyl acrylate and/or butyl acrylate and/or ethyl acrylate as the "plasticizer" component, hydroxyethyl (meth)acrylate and/or hydroxypropyl

5 (meth)acrylate, acrylic acid and/or methacrylic acid and an amide and/or an N-methylolamide and/or an etherified N-methylolamide of an α, β -unsaturated carboxylic acid in the aqueous phase in the presence of an emulsifier and a radical-forming initiator, which comprises copolymerizing

10 a mixture of

I. ~~40~~³⁰-60% by weight of methyl methacrylate or styrene or a mixture of these monomers,

II. 30-50% by weight of ethyl acrylate, butyl acrylate or 2-ethylhexyl acrylate or a mixture of these monomers,

15 III. 5-15% by weight of hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate or hydroxypropyl methacrylate or a mixture of these monomers,

IV. 1-5% by weight of acrylic acid or methacrylic acid or a mixture of these monomers and

20 V. 0.5-5% by weight of an amide or N-methylolamide or an etherified N-methylolamide of an α, β -unsaturated carboxylic acid or a mixture of monomers of this type.

The invention also relates to the use of the copolymer dispersion, obtained by this process, for the preparation of coatings which can be crosslinked under the action of heat.

25 Methyl methacrylate is preferably used as the hardening component I. Styrene can also be used alone. With regard to the resistance to weathering, in particular the UV stabi-

lity, the amount of styrene should advantageously not be more than 30% by weight relative to the total amount of monomers.

The process of polymerization according to the invention is carried out as an emulsion polymerization in an aqueous medium in the known equipment, for example in a vessel provided with a stirrer ^{and} having arrangements for heating and cooling. The addition of the monomers can be carried out in such a manner that a solution of the total water, the emulsifier and a part of the initiator is initially introduced and the mixture of monomers and, separate from but in parallel to this, the remainder of the initiator are slowly added at the polymerization temperature. However, it is also possible initially to introduce a part of the water and the emulsifier and to prepare a pre-emulsion from the remainder of the water and the emulsifier and from the monomers, which pre-emulsion is introduced into the polymerization medium, the initiator again being added separately. The polymerization is preferably carried out in such a manner that 30-50% by weight of the water and 10-50% by weight of the emulsifier or, if appropriate, mixture of emulsifiers, are initially introduced and a pre-emulsion is prepared from the monomers, the remaining part of the water and the residual emulsifiers, which pre-emulsion is metered into the heated material which has been initially introduced over 1-3 hours. The polymerization temperature is in the range from 20 to 100°C, preferably 40 to 90°C.

The ratio of the amounts of the monomers and the water is selected so that the resulting copolymer dispersion

has a solids content of 30 to 60% by weight, preferably 35 to 50% by weight.

The emulsifier employed is preferably a single anionic emulsifier or a mixture of several anionic emulsifiers. Examples of anionic emulsifiers are the alkali metal salts of the hemisulfates of alkylphenols or alcohols, and also the hemisulfates of oxethylated alkylphenols or oxethylated alcohols, preferably the alkali metal salts of the hemisulfate of a nonylphenol which has been reacted with 4-5 moles of ethylene oxide per mole, and also alkyl sulfonate or aryl sulfonate, sodium lauryl sulfate, sodium laurylethoxylate sulfate and secondary sodium alkane-sulfonates, the carbon chains of which contain 8-20 carbon atoms. The amount of the anionic emulsifier is 0.1-5.0% by weight, preferably 0.5-3.0% by weight, relative to the monomers. In addition, in order to increase the stability of the aqueous copolymer dispersion, it is possible also to employ a non-ionic emulsifier of the type of an ethoxylated alkylphenol or fatty alcohol, for example the addition product of 1 mole of nonylphenol and 4-30 moles of ethylene oxide mixed with an anionic emulsifier, also in an amount of 0.1-5.0, preferably 0.5-3.0% by weight, relative to the monomers.

The process according to the invention is carried out in the presence of a radical-forming initiator, in particular a peroxide compound. The initiator is soluble in water or in monomers. A water-soluble initiator is preferably used.

Suitable initiators are the customary inorganic

per-compounds, especially ammonium peroxydisulfate or alkali metal peroxydisulfates, for example sodium peroxydisulfate and potassium peroxydisulfate, also ammonium or alkali metal peroxydiphosphate and organic peroxides, for example, benzoyl peroxide, and also organic peresters, such as perisopivalate, to some extent in combination with reducing agents, such as sodium disulfite, hydrazine, hydroxylamine and with catalytic amounts of accelerators, such as iron, cobalt, cerium and vanadyl salts.

In order to regulate the molecular weight, compounds are employed which can be used as chain terminators in the polymerization of acrylate monomers. Apart from perhalogenated hydrocarbons, any compound having the general formula $R-SH$ (R = alkyl, aryl or aralkyl) can be used. R is preferably an aliphatic hydrocarbon radical having 2-18 carbon atoms; examples of suitable regulators are ethyl mercaptan, n-butyl mercaptan, n-octyl mercaptan, lauryl mercaptan and t-dodecyl mercaptan. The regulator is employed in an amount of 0.01-5.0% by weight, preferably of 0.5-3.0% by weight, relative to the total of the monomers. If a particularly high molecular weight is demanded for certain areas of use, the emulsion polymerization is carried out without a regulator.

After completion of the addition of the mixture of monomers, the total batch is stirred for a further 1-3 hours at 60-90°C, preferably at 70-85°C. Subsequently, the dispersion is adjusted to a pH of 7.5-9.5 with a tertiary amine, for example triethylamine, diethanolmonomethylamine, triethanolamine, dimethylisopropylhydroxy-

methyllamine, dimethylaminoethanol, dimethylaminopropanol or diethylaminoethanol. A particularly good pigment wetting of the dispersions, and thus good technological coating properties, are obtained particularly by the use of diethanolmonomethylamine, dimethylaminoethanol and dimethylaminopropanol.

The copolymers obtained by the process according to the invention have glass transition temperatures (T_G) in the range from 0 to +60°C, preferably from +5 to +35°C. The minimum film-formation temperatures (MFT) of the present aqueous copolymer dispersions correlate very well with the measured T_G values which are measured by the method of differential thermal analysis (DTA) on dried dispersion films. The process according to the invention leads to copolymers which have a mean particle size (particle diameter) of 0.05 to 0.15 μm , preferably of 0.07 to 0.12 μm .

The aqueous copolymer dispersion obtained according to the invention when mixed with a water-soluble and/or water-dispersible aminoplast resin, provides thermosetting coatings which provide fillers, texturing coatings, top coats and single-layer coatings which are particularly elastic and have particularly high adhesion, corrosion resistance and weathering resistance.

Aminoplast resins are understood to be thermosetting reaction products of aldehydes, preferably formaldehyde, with polyfunctional amines, for example urea, and triazines, such as melamine or benzoguanamine. These resins are frequently etherified, for example with methanol, in order to promote the solubility in water. A melamine resin

which is frequently used is hexamethoxymethylmelamine, which gives clear solutions in water and thus can be metered especially easily and leads to binder mixtures having good storage stability.

5 In addition, conventional alkylated, for example butylated, melamine-formaldehyde resins can be used, provided that they satisfy the requirements of water-solubility, of compatibility or of dispersibility in the finished formulation of the coating system.

10 The aqueous copolymer dispersions obtained according to the invention are mixed with the aminoplast resin in such a manner that (relative to the total resin solids) 5-40% by weight of aminoplast resin, preferably 10-30% by weight, are contained in the binder mixture.

15 The copolymer dispersions can be formulated with aminoplast resins to give transparent lacquers or pigmented lacquers. The procedure for the manufacture of the lacquers is frequently such that pigments and/or fillers, together with customary lacquer auxiliaries, optionally curing
20 catalysts and optionally neutralizers, are ground to a pigment paste which is then mixed with the binder system. However, it is frequently also possible for the aminoplast resin to serve as grinding resin (pigment wetting agent) in the manufacture of the pigment paste.

25 All the products customary in the paint and varnish industry can be employed as pigments and/or fillers, providing that they are sufficiently stable under alkaline conditions, so that the finished coating agent can be stored for several months. The pigment can be added to

the batch in the manner customary in the manufacture of pigmented aqueous emulsion paints. In lacquer formulations with aqueous copolymer dispersions, the gloss is frequently improved if the pigment is milled into the aminoplast resin and then the aqueous pigment paste is mixed into the aqueous copolymer dispersion. An example of a typical pigment for manufacturing white lacquers is titanium dioxide.

It has been found furthermore, that the copolymer dispersions prepared according to the invention have an inherent pigment-wetting capacity which is particularly pronounced. Thus it has been demonstrated, in particular, that these dispersions with inorganic white pigments, such as titanium dioxide up to a weight ratio of binder : pigment = 1 : 1, can be processed as baking coatings of high gloss and free of blooming. Reactive copolymer dispersions cross-linking foreign substances and having a similar polymeric structure which are hitherto known show, at this level of pigmentation, either a marked blooming or they can only be used with severe losses of gloss. The graphical representation is intended to illustrate this in more detail (cf. Figure).

Lacquers have been prepared as in use example 1 using a dispersion prepared according to the invention as in example 3 and various dispersions according to German Offenlegungsschrift 2,709,308. The lacquers were tested for blooming and gloss. In the Figure, the reflection (%) is plotted as a function of the level of pigmentation (%) and the assessment of the bloom is indicated at each measured point (numbers in brackets: 0 = best value possible,

5 = lowest value possible). Curve A shows the measured points for the lacquer prepared according to the invention, whilst curves B to E represent the measured points for the lacquers obtained according to the state of the art.

5 Apart from the aminoplast resins, various products can be employed as the pigment wetting agent; natural or synthetic polymers, which are dilutable with water or soluble in water, are mostly used, the affinity for water of which is achieved by a relatively large number of hydro-
10 philic components in the molecule. According to German Offenlegungsschrift 2,505,829, for example, high-boiling adducts having a molecular weight of 300-6,000 of aliphatic polyhydric alcohols and epoxides are employed.

15 In the formulation of pigmented coating compositions, it is frequently necessary also to employ so-called dispersants. In this context, the action of the dispersant on the properties of the finished film must be taken into account, for example the action on the water-resistance. The dispersants employed are, for example,
20 the ammonium salts or alkali metal salts of polymeric carboxylic acids. The amount of dispersants used depends on the type and the amount of the pigments employed and the binders.

25 The finished formulations of the coating agent can also have a tertiary amine added to increase the storage stability. The preferred pH range is 7-9.

 In order to decrease the baking temperature, the coating agent can also be mixed with a curing catalyst. A catalyst which is frequently used is paratoluenesulfonic

acid.

The coating agent based on the copolymer dispersion obtained according to the invention can be applied to a large number of substrates, which must, of course, be stable at the baking temperature. For this reason, metallic substrates are particularly suitable, for example objects made of iron, steel, aluminum, copper, bronze and brass. Ceramic surfaces, glass and wood can also be coated.

Dispersion lacquers can, for example, be applied to the substrates using spray guns, or by brush, squeegee, roller or by dipping. In practice, the coated object is principally aired and dried in air at room temperature or at a temperature which is only slightly elevated. Then the coating is cured by "baking" at a temperature from 80°-180°C. The coatings are baked, as a rule, for a period of 10-30 minutes. The layer thicknesses of the baked coatings are in the range from 15 to 80 μm , preferably 25 to 60 μm .

Baked transparent lacquer films and pigmented lacquer films based on the copolymer dispersion prepared according to the invention are distinguished by good leveling, good covering power, smoothness, elasticity, gloss, adhesion and resistance to weathering and yellowing.

The following examples serve to illustrate the invention in more detail. Percentages and ratios relate, in each case, to the weight, the amounts of solutions and dispersions relate, in each case, to the solid material.

The polymerization experiments were carried out in a multineck flask having a stirrer, thermometer,

dropping funnel and a thermostat-ed bath.

If a mercaptan is used as the regulator, care should be taken that the mercaptan is added to the mixture of monomers or the pre-emulsion of monomers only shortly before the start of the metering-in, since if the mixture or pre-emulsion of monomers containing the mercaptan is allowed to stand for any length of time, a yellow or brown coloration occurs.

Example 1

10 A monomer emulsion was prepared from
 1,150 g of methyl methacrylate
 1,150 g of 2-ethylhexyl acrylate
 250 g of hydroxyethyl methacrylate
 30 g of N-methylolacrylamide
15 20 g of methacrylamide
 50 g of methacrylic acid
 90 g of sodium lauryl sulfate
 6 g of ammonium peroxydisulfate and
 1,330 g of water.

20 This emulsion was metered into a solution of 50 g of sodium lauryl sulfate and 3 g of ammonium peroxydisulfate in 1,100 g of water. The addition time at +80°C was 2 hours and the subsequent heating time at 85°C was 3 hours. The copolymer dispersion was adjusted to pH 8 with an aqueous
25 solution of dimethylaminoethanol (25% strength). The copolymer dispersion had a solids content of 50%.
 $T_g = +14^\circ\text{C}$, $MFT = +11^\circ\text{C}$.

Example 2

A monomer emulsion composed of

100 g of styrene
1,150 g of methyl methacrylate
1,060 g of 2-ethylhexyl acrylate
250 g of hydroxyethyl methacrylate
5 50 g of methacrylic acid
30 g of N-methylolacrylamide
50 g of sodium laurylethoxylate sulfate (2-5
moles of ethylene oxide)
5 g of ammonium peroxydisulfate and
10 1,400 g of water

was metered into a solution of 30 g of sodium laurylethoxy-
late sulfate with 2-5 moles of ethylene oxide and 3 g of
ammonium peroxydisulfate in 1,100 g of water. The addition
time and the subsequent heating time were set as in Example
1. The neutralized copolymer dispersion had a solids content
15 of 50%.

$T_g = +12^{\circ}\text{C}$, $MFT = +10^{\circ}\text{C}$.

Example 3

The procedure was carried out as in Example 1, but
20 the following mixture was used:

138 g of methyl methacrylate
138 g of 2-ethylhexyl acrylate
35 g of hydroxyethyl methacrylate
7 g of methacrylic acid
25 4 g of N-methylolacrylamide
3 g of sodium laurylethoxylate sulfate (2-5
moles of ethylene oxide)
1 g of ammonium peroxydisulfate and
157 g of water.

The mixture was metered into a solution of 2 g of sodium laurylethoxylate sulfate and 0.5 g of ammonium peroxydisulfate in 135 g of water. The mixture was adjusted to pH 8.2 with dimethylaminoethanol. The copolymer dispersion had a solids content of 50%. The mean particle diameter of the copolymer was 0.080 μm .

$T_g = +14^\circ\text{C}$, MFT = $+12^\circ\text{C}$.

Example 4

An emulsion was prepared from
540 g of methyl methacrylate
360 g of 2-ethylhexyl acrylate
70 g of hydroxyethyl methacrylate
30 g of methacrylic acid
8 g of methacrylamide
10 g of sodium lauryl sulfate
3 g of lauryl mercaptan
2 g of ammonium peroxydisulfate and
470 g of water

and metered into a solution of 6 g of sodium lauryl sulfate and 1 g of ammonium peroxydisulfate in 435 g of water. The dispersion was brought to pH 8 with dimethylisopropylhydroxymethylamine and had a solids content of 50%.

$T_g = +34^\circ\text{C}$, MFT = $+32^\circ\text{C}$.

Example 5

A monomer emulsion was prepared from
360 g of methyl methacrylate
320 g of butyl acrylate
70 g of hydroxyethyl methacrylate
20 g of methacrylic acid

20 g of N-methylolacrylamide

20 g of methacrylamide

12 g of sodium laurylethoxylate sulfato (2-5
moles of ethylene oxide)

5 18 g of lauryl mercaptan and

900 g of water

and metered into a solution of 12 g of sodium lauryl sul-
fate in 600 g of water. As the initiator, a solution of
2 g of ammonium peroxydisulfate in 40 g of water was added
10 in parallel to the monomer emulsion. After adjusting the
pH to 8.5 with dimethylaminoethanol, a dispersion having
a solids content of 35% was obtained. The mean particle
diameter of the copolymer was 0.12 μ m.

Use Example 1

15 Preparation of a white lacquer paint based on the
dispersion according to Example 5:

A) Pigment paste

4.82 g of hexamethoxymethylmelamine (50% in water)

4.82 g of water (deionized)

20 1.20 g of sodium nitrite (5% in water)

0.36 g of sodium polyacrylate (25% in water)

0.19 g of addition product of 1 mole of nonyl-
phenol and 6-10 moles of ethylene oxide

0.07 g of commercial defoamer and

25 19.29 g of titanium dioxide (rutile type)

B) Binder

62 g of dispersion according to Example 5 (35%
strength) and

7.25 g of water

Part A) was initially milled in a ball mill for 16 hours, then part B) was mixed in and the mixture was again ground for a further 16 hours in a ball mill.

The white lacquer had a flow viscometer time of 30 seconds (DIN cup, DIN 53,211, 4 mm nozzle) and was adjusted to a flow viscometer time of 18-20 seconds with a mixture of water and butylglycol (7:3). The lacquer ready for spraying had a binder/pigment ratio of 1:0.8 and a solids ratio of dispersion to melamine resin of 9:1 with a solvent content of less than 2%. Lacquer films on steel plate exhibited a gloss of 85% (measured at an angle of 60 degrees in accordance with DIN 67,530). All tests of adhesion on slow and sudden deformation of the substrate and by the grid cutting process led to very good values.

Use Example 2

Preparation of a gray spray filler based on the polymer dispersion according to Example 3:

A) Pigment paste

80 g of titanium dioxide (rutile type)

40 g of talc

80 g of zinc sulfide/barium sulfate

60 g of chalk

19 g of silica gel

10 g of strontium chromate

1.5 g of flame soot

10 g of lead silicochromate

8 g of sodium polyacrylate (25% in water)

4 g of addition product of 1 mole of nonylphenol
and 6 to 10 moles of ethylene oxide

1 g of commercial defoamer
10 g of sodium nitrite (10% in water)
20 g of butylglycol and
86.5 g of water (deionized)

5 8) Binder

540 g of dispersion according to Example 3, 50%
strength, and

30 g of hexamethoxymethylmelamine.

A spray filler, which had a ratio of copolymer to
10 melamine resin of 9:1 and a ratio of binder to pigment of
1:1, was prepared by the process according to Use Example
1. The filler paint was sprayed onto steel plate and baked
at +150°C for 20 minutes. The dispersion filler films
showed good mechanical properties and good resistance pro-
15 perties on testing with chemicals (solvents and salt sol-
utions). The adhesion to conventional baking substrates
corresponded to the state of the art.

Use Example 3

Preparation of a white lacquer paint for single-
20 layer coating based on the copolymer dispersion according
to Example 3:

A) Pigment paste

100 g of titanium dioxide (rutile type)
40 g of hexamethoxymethylmelamine (50% in water)
25 3 g of sodium polyacrylate (25% in water)
1.6 g of addition product of 1 mole of nonyl-
phenol and 6-10 moles of ethylene
oxide
0.6 g of commercial defoamer

10 g of sodium nitrite (5% in water/ethanol 1:1)

and

23 g of butylglycol/ethyldiglycol (12:11).

B) Binder

5 360 g of copolymer dispersion according to

Example 3, 50% strength, and

70 g of water/butylglycol (7:3)

A white lacquer paint was prepared by the process according to Use Example 1, which paint had a flow viscometer time of 30 seconds (according to DIN 53,211), a solids content of 49% and a solvent content of less than 10%. The baked lacquer films on steel plate showed outstanding adhesion and elasticity properties:

Erichsen cupping test (DIN 53,156): 9.8 mm

15 Impact cupping test (ASTM G 14): 92 cm.kg

Grid cutting test (DIN 53,151): 0

The white lacquer films had smooth flaw-free surfaces and a gloss of 85% (DIN 67,530).

Use Example 4

20 Preparation of a gray texturing lacquer based on the copolymer dispersion according to Example 3:

A) Pigment paste

12 g of titanium dioxide (rutile type)

1.5 g of talc

25 17 g of calcium carbonate

0.2 g of soot

0.3 g of red iron oxide

1.5 g of sodium nitrite (10% in water) and

1.2 g of ethylene glycol

B) Binder

61 g of copolymer dispersion and
5.3 g of hexamethoxymethylmelamine (63% in water/
ethylene glycol, 1:1).

5 The texturing lacquer had a solids content of 65%
and a flow viscometer time of 210 seconds (according to
DIN 53,211). The ratio of binder to pigment was 1:0.9.
In order to form optimum textures, the lacquer was sprayed
on in two layers. The undercoat was diluted with water to
10 a flow viscometer time of 20 seconds (according to DIN
53,211) and then applied. After an airing period, the
actual texturing lacquer was sprayed on undiluted. The
formation of texture with the copolymer dispersion accord-
ing to Example 3 as the binder was significantly better
15 than that with conventional alkyd resin binders.

Use Example 5

Preparation of a red single-layer lacquer based
on the copolymer dispersion according to Example 4:

A) Pigment paste

20 38 g of molybdate red
19 g of permanent red
3 g of sodium polyacrylate (25 % in water)
15 g of sodium nitrite (10% in water)
65 g of ethylene glycol
25 3 g of dimethylaminoethanol and
105 g of water (deionized).

B) Binder

684 g of copolymer dispersion
60 g of hexamethoxymethylmelamine (63% in water/

ethylglycol, 1:1) and

8 g of commercial silicone-based leveling
auxiliary (50% in solvent)

A red lacquer paint, which had a ratio of polymer
5 to melamine resin of 9:1 and a ratio of binder to pigment
of 1:0.15, was prepared by the process according to Use
Example 1. At a solids content of 44% and a pH of 8.5,
the flow viscometer time of the dispersion was 17 seconds
(DIN 53,211). The proportion of organic solvents was 8%.
10 The lacquer films baked at 130°C (30 minutes) had gloss
values of 86-88% (DIN 67,530). The exceptional adhesion
was also demonstrated by a value of 9.2 mm in the Erichsen
cupping test (DIN 53,156).

Comparison Example to Use Example 3

15 Preparation of white lacquer paints for single-
layer coatings based on copolymer dispersions according to
German Offenlegungsschriften 2,211,169 (Example 2) and
2,709,308 (Example 1, 47% strength):

A) Pigment paste

20 64 g of titanium dioxide (rutile type)
16 g of hexamethoxymethylmelamine (50% in water)
1.2 g of sodium polyacrylate (25% in water)
0.64 g of addition product of 1 mole of nonyl-
phenol and 6-10 moles of ethylene oxide
25 0.24 g of commercial defoamer and
4 g of sodium nitrite (5% in water/ethanol,
1:1).

B) Binder

152 g of copolymer dispersion.

In the process of preparation of the white lacquers in a ball mill, with the dispersion according to German Offenlegungsschrift 2,211,169, stable lacquer paints were not obtained. The pigment wetting was insufficient and the
5 lacquer paint contained pigment agglomerates. Spray application was not possible because of the deficient homogeneity of the lacquer.

With the dispersion according to German Offenle -
gungsschrift 2,709,308, a stable white lacquer was obtained,
10 but this, after spray application and baking, led to lacquer surfaces which were very irregular (pits, blisters and pin-holes) and which had inadequate resistance to chemicals and gloss values of 70% (according to DIN 67,530).

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the preparation of an aqueous dispersion of copolymers, which can be crosslinked with aminoplasts by the action of heat, by copolymerization of (A) styrene and/or methyl methacrylate, (B) 2-ethylhexyl acrylate and/or butyl acrylate and/or ethyl acrylate, (C) hydroxyethyl (meth)acrylate and/or hydroxypropyl (meth)acrylate, (D) acrylic acid and/or methacrylic acid and (E) an amide and/or an N-methylolamide and/or an etherified N-methylolamide of an α,β -unsaturated carboxylic acid in the aqueous phase in the presence of an emulsifier and a radical-forming initiator, which comprises copolymerizing a mixture of

- I. ³⁰~~10~~-60% by weight of methyl methacrylate or styrene or a mixture of these monomers,
- II. 30-50% by weight of ethyl acrylate, butyl acrylate or 2-ethylhexyl acrylate or a mixture of these monomers,
- III. 5-15% by weight of hydroxyethyl acrylate, hydroxy-ethyl methacrylate, hydroxypropyl acrylate or hydroxypropyl methacrylate or a mixture of these monomers,
- IV. 1-5% by weight of acrylic acid or methacrylic acid or a mixture of these monomers and
- V. 0.5-5% by weight of an amide or N-methylolamide or an etherified N-methylolamide of an α,β -unsaturated carboxylic acid or a mixture of monomers of this type.

2. A process according to claim 1 wherein component I is methyl methacrylate.
3. A process according to claim 1 wherein component I is styrene alone which is present in an amount not more than 30% by weight relative to the total amount of monomers.
4. A process according to claim 1, 2 or 3 wherein the ratio of the amounts of monomers and water is selected so that the resulting copolymer dispersion has a solids content of 30 to 60% by weight.
5. A process according to claim 1, 2 or 3 wherein the ratio of the amounts of monomers and water is selected so that the resulting copolymer dispersion has a solids content of 35 to 50% by weight.
6. A process according to claim 1, 2 or 3 wherein after completion of addition of the monomers the total batch is stirred for a further 1-3 hours at 60° - 90°C and the pH is then adjusted to a value in the range 7.5-9.5 with a tertiary amine.
7. A process according to claim 1, 2 or 3 wherein after completion of addition of the monomers the total batch is stirred for a further 1-3 hours at 60° - 90°C and the pH is then adjusted to a value in the range 7.5-9.5 with a tertiary amine selected from the group consisting of triethylamine, diethanolmonomethylamine, triethanolamine, dimethylisopropylhydroxymethylamine, dimethylaminoethanol, dimethylaminopropanol and diethylaminoethanol.

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8. A coating composition which can be crosslinked by the action of heat, which composition comprises an aqueous dispersion of copolymers made by a process according to claim 1 and a water-soluble or water dispersible aminoplast resin.

9. A process for preparing a coating composition which can be crosslinked by the action of heat, which comprises admixing an aqueous dispersion of copolymers made by a process according to claim 1 with a water-soluble or water-dispersible aminoplast resin.

10. A method of coating a substrate which comprises applying to the substrate a coating composition as claimed in claim 8, drying the coated substrate and then curing the coating by baking at a temperature of from 80 to 180°C for 10-30 minutes.

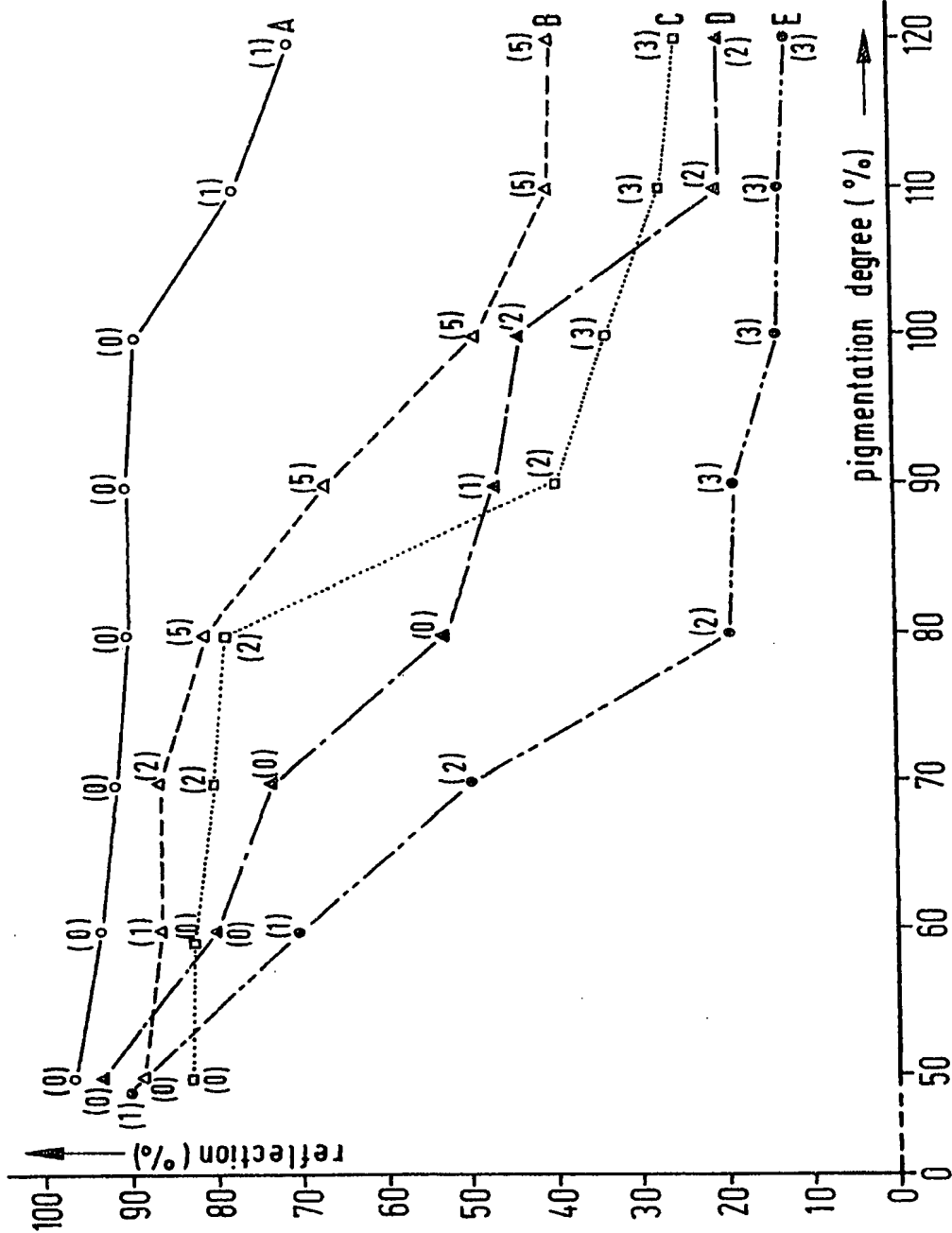
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